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# Continuous Hydrothermal Synthesis of Metal Germanates ( $M_2GeO_4$ ; $M = Co, Mn, Zn$ ) for High Capacity Negative Electrodes in Li-ion Batteries

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## Abstract

Nanosized metal germanates ( $M_2GeO_4$ ;  $M = Co, Mn, Zn$ ) were synthesised using a continuous hydrothermal flow synthesis process for the first time. Phase-pure rhombohedral  $Zn_2GeO_4$  nanorods, cubic spinel  $Co_2GeO_4$  nanoparticles, and orthorhombic  $Mn_2GeO_4$  nanotubes/nanoparticles were obtained. The electrochemical properties of all samples as active materials for negative electrodes in Li-ion half cells was explored. The galvanostatic and potentiodynamic testing was conducted in the potential range 3.00 to 0.05 V vs.  $Li/Li^+$ . The results suggest that both alloying and conversion reactions associated with Ge contributed to the stored charge capacity;  $Zn_2GeO_4$  showed a high specific capacity of 600 mAh  $g^{-1}$  (10 cycles at 0.1 A  $g^{-1}$ ) due to alloying and conversion reactions for both Ge and Zn.  $Mn_2GeO_4$  was studied for the first time as a potential negative electrode material in a Li-ion half-cell; an excellent specific charge capacity of 510 mAh  $g^{-1}$  (10 cycles / 0.1 A  $g^{-1}$ ) was obtained with a significant contribution to charge arising from the conversion reaction of Mn to MnO upon delithiation. In contrast,  $Co_2GeO_4$  only showed a specific capacity of 240 mAh  $g^{-1}$ , after 10 cycles at the same current rate, which suggested that cobalt had little or no benefit for enhancing stored charge in the germanate.

**Keywords:** Alloying material, ternary oxide, germanate, negative electrode

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## Introduction

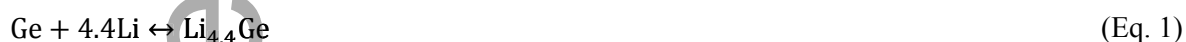
Growing awareness of anthropomorphic climate change due to greenhouse gases has made research of secondary Li-ion battery (LIB) increasingly relevant.<sup>[1]</sup> The major advantage of LIBs over other electrochemical energy storage technologies is their superior energy densities.<sup>[2]</sup> Whilst most commercial LIBs employ graphite as active material in the negative electrode, many other active materials have been proposed to improve upon some of the detrimental properties of graphite; safety concerns because of potential cell failure due to lithium dendrite formation,<sup>[3]</sup> irreversible capacity losses during the first cycle,<sup>[3,4]</sup> and poor rate performance.<sup>[4]</sup>

Lithium insertion materials including some transition metal oxides, have been studied as active materials with superior rate performance.<sup>[5]</sup> When specific capacity is the major focus, alloying materials such as Si, Sn, and ternary oxides are generally considered.<sup>[6,7]</sup> Graphite has a theoretical capacity of 372 mAh g<sup>-1</sup> (1 Li<sup>+</sup> per six C), whereas alloying materials have theoretical capacities of up to 3572 mAh g<sup>-1</sup> (for silicon, 15 Li<sup>+</sup> per Si).<sup>[7,8]</sup> The major disadvantages of alloying active materials, however, have been reported to be poor rate performance due to the diffusion-limited nature of the alloying process and large capacity fading due to the substantial volume changes upon lithiation/delithiation.<sup>[6,9,10]</sup> However, it has previously been reported that morphology can significantly influence the cycling performance of alloying Li-ion battery active materials,<sup>[11]</sup> and that nanostructure<sup>[12]</sup> and core-shell designs<sup>[13]</sup> can improve electrochemical cycling stability.

Transition metal oxides such as manganese oxides, iron oxides, cobalt oxides, and nickel oxides are known to undergo conversion reactions upon lithiation. The metals are reduced to an oxidation state of 0, whereas the oxygen forms lithium superoxide (Li<sub>2</sub>O) with lithium ions.<sup>[12]</sup> Although these materials can show high reversible specific capacities, they

typically suffer from large voltage hysteresis,<sup>[14]</sup> low energy efficiencies,<sup>[15]</sup> large capacity fading, and poor rate performance.<sup>[2]</sup> Ternary mixed-metal oxides such as ferrites, cobaltites, and germanates have been suggested as possible alternatives to Si or Sn because of high ionic transport coefficients, high electronic conductivity, and relatively simple synthesis methods.<sup>[12]</sup>

Elemental Ge has received interest as a potential alloying active material for LIB negative electrodes because of its relatively high theoretical capacity ( $1384 \text{ mAh g}^{-1}$ ),<sup>[16]</sup> the significantly higher diffusivity of  $\text{Li}^+$  in Ge compared to the more commonly studied Si (up to 400 times higher at room temperature),<sup>[17]</sup> as well as its significantly higher electronic conductivity compared to Si (up to 10 000 times higher at room temperature).<sup>[18]</sup> However, Ge suffers from large volume changes upon lithiation (260 %),<sup>[19]</sup> which occurs according to Equation 1:<sup>[20]</sup>



Because Ge is expensive compared to some other transition metal oxides,  $\text{GeO}_2$  (germania) has been considered because of its lower cost. Upon the first lithiation, germania is irreversibly reduced to elemental Ge as shown in equation 2:<sup>[16]</sup>



Upon further lithiation, reversible alloying of Ge with Li occurs according to Eq. 1. Whilst Eq. 1 and Eq. 2 give theoretical reversible gravimetric and volumetric capacities of  $1100 \text{ mAh g}^{-1}$  and  $4\,653 \text{ mAh cm}^{-3}$ , respectively (much higher than those for graphite),<sup>[16]</sup> however, capacity retention in germania has been reported to be inadequate.<sup>[21]</sup>

To overcome both the poor cyclability and high cost of Ge and  $\text{GeO}_2$ , metal germanates  $\text{M}_2\text{GeO}_4$  (M = e.g. Zn, Co, Fe, etc.) have been studied as active negative electrode materials.  $\text{Zn}_2\text{GeO}_4$  is of interest because of the high theoretical capacity of 1443

$\text{mAh g}^{-1}$ , which is a result of the electrochemical activity of both Zn and Ge species via alloying (as the metal) or conversion reactions (as the oxides).<sup>[22,23]</sup>  $\text{Co}_2\text{GeO}_4$  has been studied because of the complementary conversion reaction of Co with  $\text{Li}_2\text{O}$ , which can occur at higher potentials vs.  $\text{Li/Li}^+$  than the alloying/dealloying reaction of Ge, which results in a highly conductive amorphous network of Co and  $\text{Li}_2\text{O}$  to improve the Ge alloying reaction.<sup>[20]</sup> Mn-doping of  $\text{Zn}_2\text{GeO}_4$  has been reported in the literature and was shown to improve the specific capacity at all applied specific currents compared to  $\text{Zn}_2\text{GeO}_4$ .<sup>[24]</sup> Morphology has also been shown to significantly influence performance, with hollow nanoparticles significantly outperforming short nanorods of  $\text{Zn}_2\text{GeO}_4$ .<sup>[11]</sup>

Whilst nanosizing the morphology of  $\text{M}_2\text{GeO}_4$  active materials has been reported to improve cycling stability, rate performance, and increase overall capacity, nanosizing often requires long synthesis steps ( $> 10$  hours),<sup>[11,23–26]</sup> multiple steps,<sup>[23,25]</sup> and is therefore limited in the potential for scalability with regular yields  $< 1 \text{ g}$ .<sup>[20,22,27]</sup> Herein we describe a scalable, single step, Continuous Hydrothermal Flow Synthesis (CHFS) process for the production of three different metal germanates ( $\text{Zn}_2\text{GeO}_4$ ,  $\text{Co}_2\text{GeO}_4$ ,  $\text{Mn}_2\text{GeO}_4$ ) with different crystal structures. The CHFS methodology was recently reviewed by the authors and has shown to be a powerful tool in the continuous preparation of oxide, sulphide, metal nanoparticles for use in Na-ion batteries, Zn-air batteries, fuel cells, photocatalysts, transparent conducting oxides, optical modifiers, pigments, antibacterials and magnetic materials among other applications.<sup>[28]</sup>

## Materials & Methods

### Chemicals

The chemicals used were of analytical grade and used without purification. The chemicals were purchased from Sigma-Aldrich, Dorset, UK, unless stated otherwise. The chemicals included  $\text{GeO}_2$  (> 99.99 %), KOH (analytical reagent grade, Fisher Chemicals, Loughborough, UK),  $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$  (zinc acetate dihydrate, analytical grade),  $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  (cobalt acetate tetrahydrate, reagent grade),  $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$  (manganese acetate tetrahydrate, > 99 %), Super P conductive carbon (Alfa Aesar, Heysham, UK), polyvinylidene fluoride (PVDF, PI-KEM, Staffordshire, UK), and N-methyl-2-pyrrolidone (NMP).

### Continuous hydrothermal flow synthesis

A continuous hydrothermal flow synthesis (CHFS) process was used to synthesise nanoparticles of  $\text{Zn}_2\text{GeO}_4$ ,  $\text{Co}_2\text{GeO}_4$ , and  $\text{Mn}_2\text{GeO}_4$ . This CHFS process has previously been described by some of the authors at both pilot scale<sup>[29]</sup> and at lab scale.<sup>[28,30–32]</sup> The process used herein was at the lab scale, a diagram of which can be found in the Supplementary information (see Figure S1). Herein, a water feed above the critical temperature and pressure of water ( $T_c = 374\text{ }^\circ\text{C}$ ;  $p_c = 22.1\text{ MPa}$ ) was mixed with an ambient temperature flow of aqueous metal salts. This flow of aqueous metal salts consisted of a flow of metal precursors for the metal germanates (consisting of the premade solution containing the Ge precursor and one of the Zn, Co, or Mn aqueous salts), which was pre-mixed with a flow of base ( $\text{KOH}_{\text{aq}}$ ). The following concentrations were used as feeds; the KOH concentration was 0.5 M, whilst for the metal feed, the [Ge] was always 0.04 M, and the [M] was 0.08 M (where M is either Co, Zn or Mn). The supercritical water feed and the ambient temperature aqueous metal salt flow were combined in a co-current, patented Confined Jet Mixer (CJM), which was made from off the shelf Swagelok<sup>TM</sup> parts.<sup>[33]</sup> The temperature at the mixing point in the CJM was 335 °C as a result of balanced flows from Pump 1 (80 mL min<sup>-1</sup>, supercritical water) and Pumps 2 and 3 (40 mL min<sup>-1</sup> each, aqueous metal precursors and KOH feeds, respectively).

After mixing in the CJM and a 5 seconds residence time, the newly formed particle slurry was cooled to ca. 40 °C in a pipe-in-pipe heat exchanger.<sup>[34]</sup> The nanoparticle slurry was collected from the outlet of the back-pressure regulator and then cleaned by dialysis using DI water for 48 hours by which time the conductivity of the water was less than 50  $\mu\text{S cm}^{-1}$ . Then, the samples were concentrated into a sludge that was freeze-dried via cooling to below -40 °C in a vacuum of 13.3 Pa using a Virtis Genesis 35XL freeze-drier (SP Scientific, Pennsylvania, US). The freeze-dried powders were used as active materials without any heat-treatment or further processing. The rate of synthesis was ca. 25 g h<sup>-1</sup> for each sample.

### **Physical characterisation**

Powder X-ray diffraction (PXRD) of all three powders was carried out in the 2 $\theta$  range 7.5 to 30.0°, using Mo-K $\alpha$  radiation ( $\lambda$  = 0.7107 Å). The step time was set to 20 s and the step size to 0.5° 2 $\theta$ . The PXRD patterns were collected on a STOE StadiP diffractometer.

High-resolution Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) were performed using a JOEL JEM 2100 with a LaB<sub>6</sub> filament for size and particle morphology analysis as well as elemental analysis and mapping, respectively. The samples were dispersing in methanol and pipetted onto a 300-mesh copper grid (Agar Scientific, Stansted, UK). A Gatan Orius digital camera was used for the image capture of the TEM micrographs.

X-ray photoelectron spectroscopy (XPS) used a Thermo Scientific K-alpha™ spectrometer (Al-K $\alpha$  radiation) with a 128 -channel position sensitive detector to analyse the valence states and concentrations of metal ions on the nanoparticle surfaces. For Ge, Zn, Mn, Co, and O, high-resolution regional scans were conducted at 50 eV. CasaXPS™ software (version 2.3.19) was used to process the data.

The Brunauer-Emmett-Teller (BET) technique was used to determine the specific surface areas of the powders. BET measurements used a Micrometrics Tristar II. Before BET measurements, the samples were degassed at 120 °C for 12 h.

### **Electrochemical characterisation**

Anodes for LIBs were prepared by mixing the corresponding metal germanate active material powder with Super P conductive carbon and PVDF binder in the wt% ratio of 80:10:10. The PVDF was added in the form of a pre-dissolved 5 wt% solution in NMP. An ink was created by the addition of more NMP (ca. 2 mL); this ink was ball-milled at 800 rpm for 1 hour and then cast onto copper foil (9 µm thickness, PI-KEM, Staffordshire, UK). The sheets were dried for 10 minutes at ca. 200 °C on a hotplate until they were superficially dry. The electrode sheets were then left to dry overnight at room temperature. After the electrodes were cut out, they were dried overnight under vacuum at 120 °C in the heated antechamber of a glovebox (MB-Unilab Plus SP, M. Braun Inertgas-Systeme, Garching, Germany). The Ar-filled glovebox ( $\text{H}_2\text{O}$  and  $\text{O}_2 < 1$  ppm) was used for cell assembly. The active mass loading of the electrodes was in the range 1.2 to 2.0 mg cm<sup>-2</sup> and their thickness was ca. 35 µm.

Li-ion half-cells in CR2032 coin cell cases were made using each of the metal germanate negative electrodes, with lithium metal discs (PI-KEM, Staffordshire, UK) as reference and counter electrodes, and Whatman GF/D glass microfiber (Buckinghamshire, UK) separators. The separators were drenched in an organic electrolyte containing 1 M LiPF<sub>6</sub> (dissolved in 1:1 volume ratio ethylenecarbonate/ethylmethylcarbonate, BASF, Ludwigshafen, Germany).

Galvanostatic and potentiodynamic cycling was carried out using an Arbin Instruments Model BT-2000 battery tester (Caltest Instruments Ltd, Guildford, UK) at room temperature in the potential range 0.05 to 3.0 V vs. Li/Li<sup>+</sup>. The galvanostatic



charge/discharge cycling was carried out at specific currents in the range 0.1 to 10.0 A g<sup>-1</sup> and long-term cycling was carried out at a specific current of 0.1 A g<sup>-1</sup>. Cyclic voltammetry (CV) was used for potentiodynamic measurements at scan rates in the range 0.05 to 100 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was performed for as-made Li-ion half-cells and for half-cells after 30 cycles of galvanostatic cycling. EIS was carried out on an Interface 1000 Gamry potentiostat (Gamry Instruments, Pennsylvania, US) in the range of frequencies 100 kHz to 10 mHz, using an AC voltage of 0.01 V rms.

## Results & Discussion

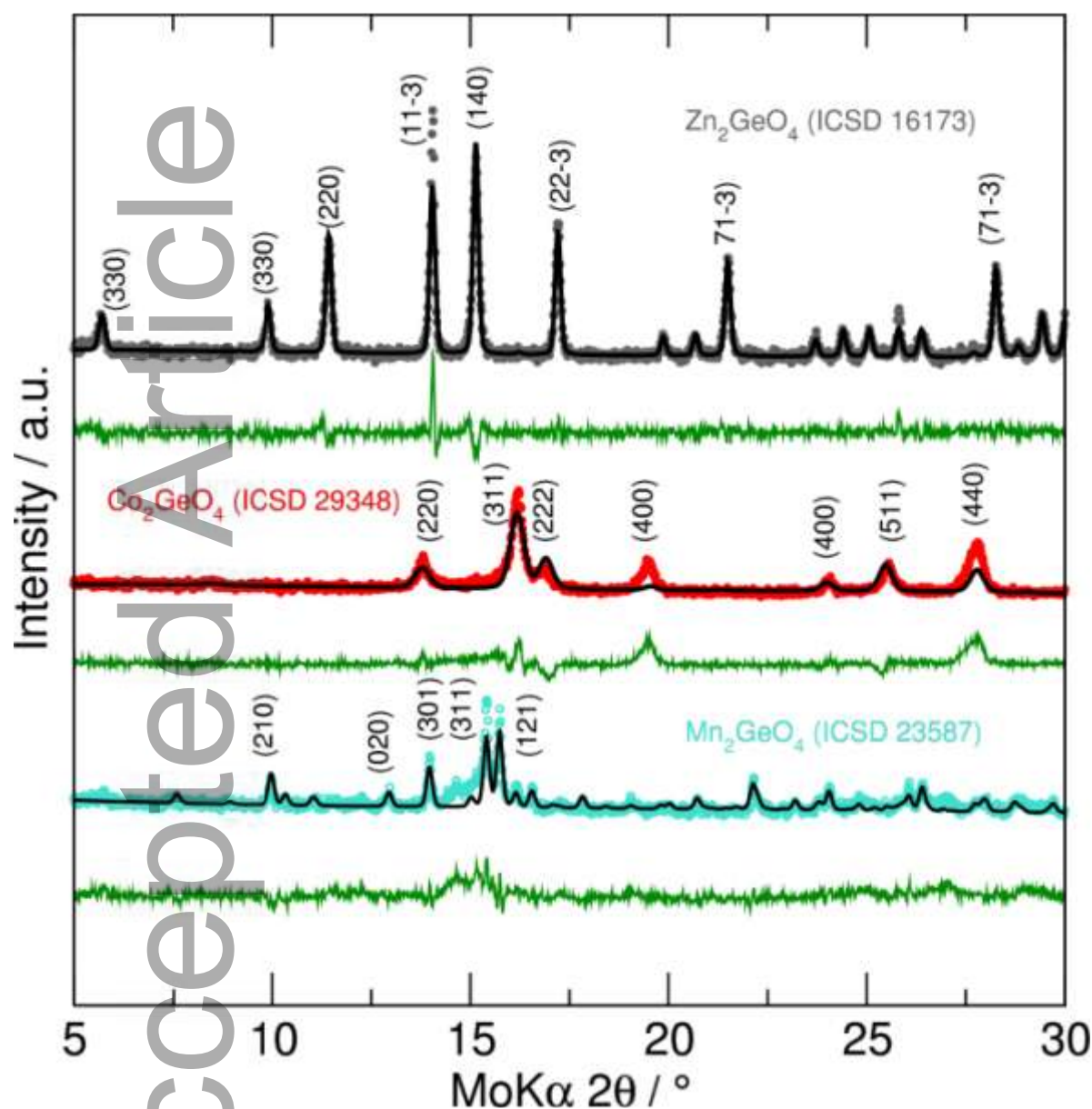


Figure 1: Powder X-ray diffraction patterns and Rietveld refinement of rhombohedral  $\text{Zn}_2\text{GeO}_4$  (ICSD no.: 16173), spinel  $\text{Co}_2\text{GeO}_4$  (ICSD no.: 29348) and orthorhombic  $\text{Mn}_2\text{GeO}_4$  (ICSD no.: 23587) prepared by a continuous hydrothermal route. Calculated fits are shown as black lines with the respective residuals below each fit in green.

The as-prepared nano-powders were recovered as white, black, and light grey powders for  $\text{Zn}_2\text{GeO}_4$ ,  $\text{Co}_2\text{GeO}_4$ , and  $\text{Mn}_2\text{GeO}_4$ , respectively. The powder X-ray diffraction (PXRD) patterns subsequent Rietveld refinement of the three samples revealed a different crystal structure for each, as expected (see Figure 1, polyhedral models of the three structures are

given in Figure S2). The pattern for  $\text{Zn}_2\text{GeO}_4$  was a good match to the reference pattern for rhombohedral  $\text{Zn}_2\text{GeO}_4$  (ICSD no. 16173; space group:  $R\bar{3}H$ ). The major peaks corresponded to the (220), (11 $\bar{3}$ ), (140), and (22 $\bar{3}$ ) planes for rhombohedral  $\text{Zn}_2\text{GeO}_4$  at  $2\theta = 11.7, 14.2, 15.3, \text{ and } 17.2^\circ$ , respectively.<sup>[24,26]</sup> The pattern for  $\text{Co}_2\text{GeO}_4$  was a good match for the reference pattern for cubic spinel  $\text{Co}_2\text{GeO}_4$  (ICSD no.: 29348; space group:  $Fd\bar{3}mS$ ). The major peaks corresponded to (311), (400), and (440) planes for cubic spinel  $\text{Co}_2\text{GeO}_4$  at  $2\theta = 16.4, 19.7, \text{ and } 27.7^\circ$ , respectively.<sup>[35]</sup> Significant peak broadening was also observed for  $\text{Co}_2\text{GeO}_4$ , suggesting a small crystallite domain size for the material. The PXRD pattern for  $\text{Mn}_2\text{GeO}_4$  showed the sharpest peaks and was a good match for orthorhombic  $\text{Mn}_2\text{GeO}_4$  (ICSD no.: 23587; space group:  $Pnma$ ). The major peaks corresponded to the (301), (311), and (121) planes of orthorhombic  $\text{Mn}_2\text{GeO}_4$  at  $2\theta = 14.2, 15.6, \text{ and } 15.9^\circ$ , respectively.

Equation 3 (Scherrer equation) was used to estimate the domain size of the synthesised particles:

$$d = \frac{K \times \lambda}{\beta \times \cos \theta} \quad (\text{Eq. 3})$$

For the Scherrer equation,  $d$  is crystallite size in nm,  $\lambda$  is the radiation source's wavelength (here Mo radiation,  $0.7107 \text{ \AA}$ ),  $\beta$  the full width at half-maximum (FWHM) of the peaks and  $\theta$  the Bragg angle. The shape factor  $k$  can range from 0.86 to 0.98, and if unknown, was approximated to 0.9.<sup>[36]</sup> The estimated domain sizes were  $24 (\pm 3)$ ,  $11 (\pm 2)$ , and  $34 (\pm 3) \text{ nm}$  for  $\text{Zn}_2\text{GeO}_4$ ,  $\text{Co}_2\text{GeO}_4$ , and  $\text{Mn}_2\text{GeO}_4$ , respectively, which confirmed the broad conclusions drawn from the peak shapes of the PXRD patterns.

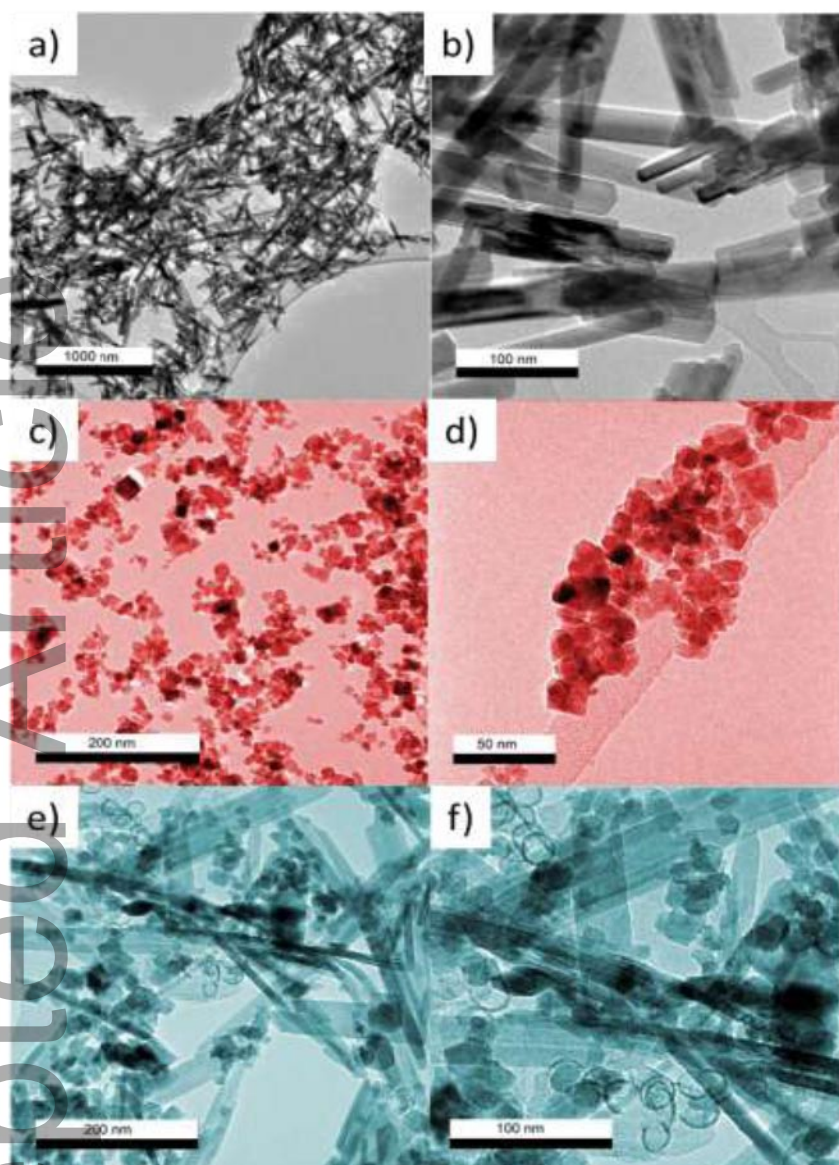


Figure 2: Transmission electron micrographs of a+b) Zn<sub>2</sub>GeO<sub>4</sub> nanorods, c+d) Co<sub>2</sub>GeO<sub>4</sub> nanoparticles, and e+f) Mn<sub>2</sub>GeO<sub>4</sub> mixed nanoparticles/nanotubes.

Rietveld refinement highlighted several discrepancies in the peak intensities for the three materials. These reflections were found to be (11-3) for Zn<sub>2</sub>GeO<sub>4</sub>, (400) and (440) for Co<sub>2</sub>GeO<sub>4</sub> and (311) and (121) for Mn<sub>2</sub>GeO<sub>4</sub> and are likely due to preferential crystal growth in particular directions. Mn<sub>2</sub>GeO<sub>4</sub> also showed a broad hump below the (311) and (121) reflections likely due to the presence of an unidentified secondary phase with low crystallinity which contributes to the lower calculated (and higher observed) reflection intensities in this material.



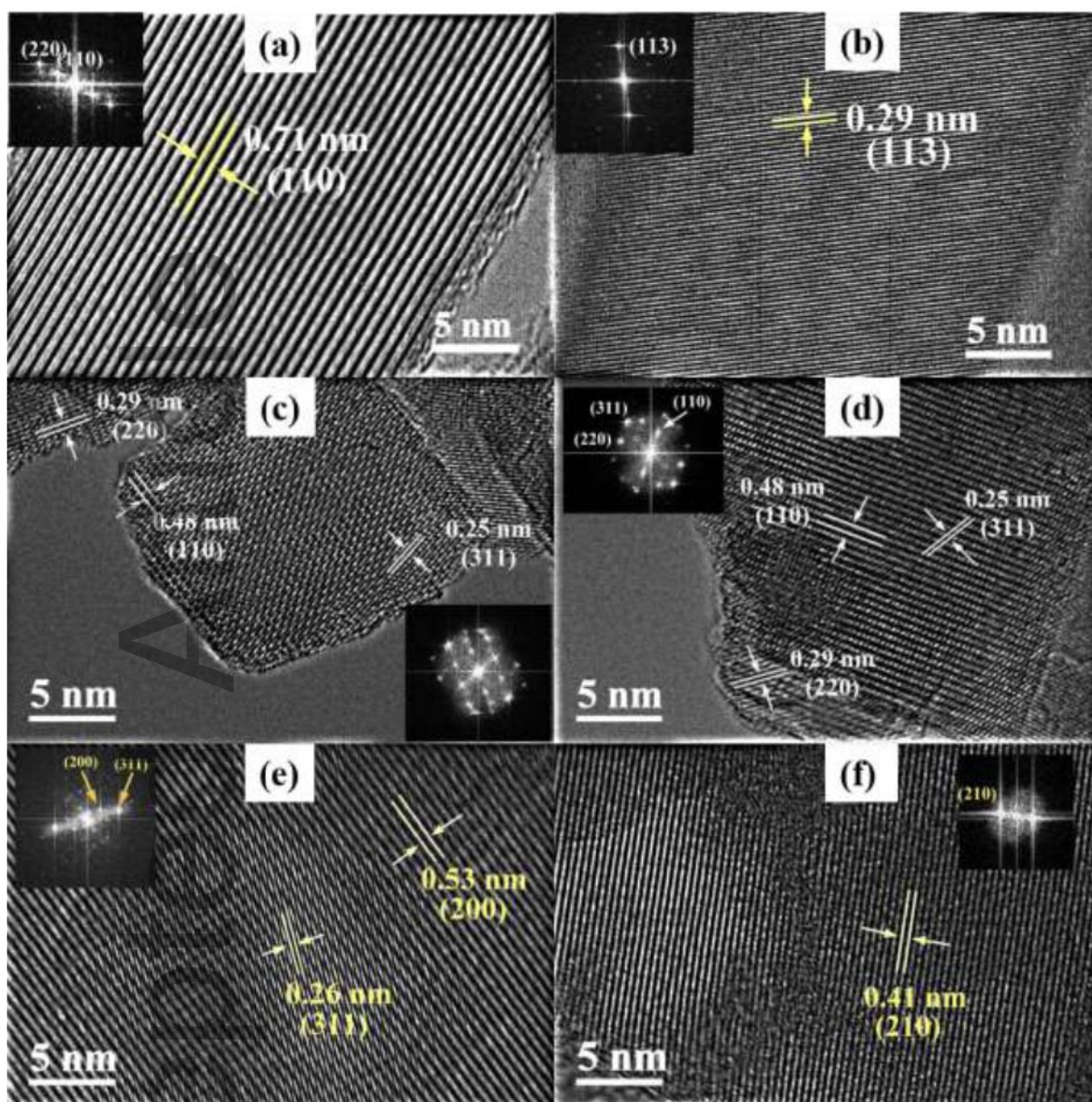


Figure 3: Hi-Resolution Transmission Electron Micrographs of (a+b)  $\text{Zn}_2\text{GeO}_4$ ; (c+d)  $\text{Co}_2\text{GeO}_4$ , and (e+f)  $\text{Mn}_2\text{GeO}_4$  nanostructures.

To investigate the potential preferential growth and size of the three germinates, transmission electron micrographs (TEM) was employed and revealed different morphologies and particle sizes for the different samples.  $\text{Zn}_2\text{GeO}_4$  presented as nanorods, with lengths varied in the range of 50 to 500 nm and widths in the range of 10 to 20 nm, with aspect ratios ranging from 1:5 to 1:30.  $\text{Co}_2\text{GeO}_4$  nanoparticles showed an average particle size of  $17 \pm 5$  nm with a variety of morphologies, although most particles were spherical or cubic.  $\text{Mn}_2\text{GeO}_4$  particles were both cube-like nanoparticles and nanotubular in structure. The

nanoparticles have an average diameter of  $28 \pm 9$  nm, while the nanotube length varied from 70 to 400 nm and widths from 10 to 60 nm. To further our understanding on the crystal structure, HRTEM was carried out on these materials. For  $\text{Zn}_2\text{GeO}_4$ , as shown in Figure 3a and b, the lattice spacings were found to be 0.71 and 0.29 nm, corresponding to (110) and (113) lattice planes, respectively. It can also be seen that the (110) plane is oriented parallel to the nanorod (growth direction) while the (113) plane is at an angle of  $66^\circ$  to the growth direction of the rod. Therefore it can be stated that the hydrothermal flow synthesis resulted in  $\text{Zn}_2\text{GeO}_4$  nanorods growing along the *c*-axis of the rhombohedral phenacite-type structure.<sup>[37,38]</sup> These  $\text{Zn}_2\text{GeO}_4$  nanorods were single crystalline in nature with no defects. Lattice fringes for  $\text{Co}_2\text{GeO}_4$  were found to be rather non-uniform. For  $\text{Co}_2\text{GeO}_4$ , three different overlapped lattices could be observed in Figure 3c and d. The measured *d* spacing of 0.48, 0.29 and 0.25 nm can be related to the (110), (220) and (311) planes of fcc  $\text{Co}_2\text{GeO}_4$  structure.<sup>[39]</sup> In the case of orthorhombic  $\text{Mn}_2\text{GeO}_4$ , with unit cell dimensions  $a = 10.7 \text{ \AA}$ ,  $b = 6.26 \text{ \AA}$  and  $c = 5.04 \text{ \AA}$ , lattice spacing for the observed peaks in the XRD pattern could be calculated to be  $d_{210} = 0.41 \text{ nm}$ ,  $d_{020} = 0.30 \text{ nm}$ ,  $d_{301} = 0.29 \text{ nm}$ ,  $d_{311} = 0.26 \text{ nm}$ ,  $d_{121} = 0.26 \text{ nm}$ ,  $d_{200} = 0.53 \text{ nm}$ . From these calculated values the observed lattice spacing of 0.26, 0.53 and 0.41 nm in Figure 3e and f can be related to the (311), (200), and (210) planes. It can be assumed that the lattices  $d_{311}$  and  $d_{121}$  have the same lattice spacing. However, by comparing the intersection angle between the lattice planes (200), (311), and (200), (121) lattices have been identified in Figure 3e. To the best of the authors' knowledge, there are no previous reports on HRTEM for  $\text{Mn}_2\text{GeO}_4$ .

Energy dispersive X-ray spectroscopy (EDX) mapping showed even distributions of the respective metal and Ge across all particles (see Figure S3). This suggested that there was no enrichment of any metal ions anywhere in or on the particles and that the materials were phase-pure. A quantitative analysis of the atomic quantities in  $\text{Zn}_2\text{GeO}_4$ , showed a concentration of  $35 (\pm 3)$  and  $65 (\pm 3)$  at% for Ge and Zn, respectively. In comparison, for

Co<sub>2</sub>GeO<sub>4</sub> and Mn<sub>2</sub>GeO<sub>4</sub>, the metal and Ge were in the at% ratios of 31(±6):69(±5) and 31(±3):69(±3), respectively. These values were in line with expectations for the synthesised materials.

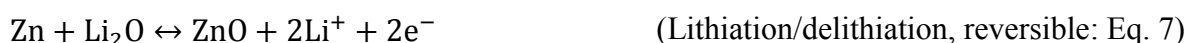
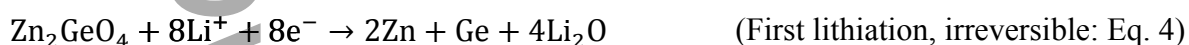
X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states and semi-quantitative atomic concentrations on the surface of the different metal germanate particles. The Zn 2*p* level binding energies showed two peaks at 1022.2 and 1045.3 eV, which were assigned to Zn 2*p*<sub>3/2</sub> and Zn 2*p*<sub>1/2</sub>, respectively (see Figure S4a). This was in good agreement with an oxidation state of Zn(II).<sup>[40]</sup> For Co 2*p* binding energies, the high-resolution spectrum showed two main peaks centred at 780.9 and 796.9 eV, corresponding to Co 2*p*<sub>3/2</sub> and Co 2*p*<sub>1/2</sub>, respectively. The two satellite peaks at 785.7 and 802.9 eV (see Figure S4b) are identifiers for Co(II) and, therefore, confirmed the expected oxidation state of Co as +2 valence.<sup>[35]</sup> For the high-resolution Mn 2*p* spectrum, the Mn 2*p*<sub>3/2</sub> and Mn 2*p*<sub>1/2</sub> peaks were centred at 641.5 and 653.3 eV, respectively (see Figure S4c). The shake-up satellite feature between the two peaks is only associated with the Mn(II) oxidation state of Mn; hence, this confirmed the expected oxidation state of Mn as +2.<sup>[41]</sup> For the Ge 3*d* spectra of the three samples, the single intense peak of Ge 3*d* centred at 32.3, 32.3, and 32.4 eV for Zn<sub>2</sub>GeO<sub>4</sub>, Co<sub>2</sub>GeO<sub>4</sub>, and Mn<sub>2</sub>GeO<sub>4</sub>, respectively (see Figure S4d), was in the location usually associated with germania and, therefore, an oxidation state of Ge(IV).<sup>[35,40]</sup> Semi-quantitative analysis of the peak areas of the spectra from XPS showed M:Ge at% ratios of 70:30 (M=Zn), 67:33 (M = Co), and 64:36 (M = Mn).

The Brunauer-Emmett-Teller (BET) N<sub>2</sub> absorption/desorption measurements revealed significant differences in specific surface areas (SSA) for the three samples (see Figure S5). The SSAs were 28, 65, and 44 m<sup>2</sup> g<sup>-1</sup> for Zn<sub>2</sub>GeO<sub>4</sub>, Co<sub>2</sub>GeO<sub>4</sub>, and Mn<sub>2</sub>GeO<sub>4</sub>, respectively. Therefore, Co<sub>2</sub>GeO<sub>4</sub> showed the highest SSA, the smallest estimated domain size, and the smallest particles according to the electron micrographs. Mn<sub>2</sub>GeO<sub>4</sub> showed the second largest

SSA, but the largest estimated domain size, however, this could have been a result of the two different morphologies of  $\text{Mn}_2\text{GeO}_4$  as observed from TEM. Finally,  $\text{Zn}_2\text{GeO}_4$  showed the largest particles in the micrographs due to the rod-like morphology and the smallest SSA; the relatively high estimated domain size aligned well with this.

### Electrochemical Characterization

To explore the lithiation and delithiation mechanisms for the half cells, potentiodynamic cyclic voltammetries and galvanostatic charge/discharge cycling were carried out in the potential window 3.00 to 0.05 V vs.  $\text{Li}/\text{Li}^+$ . The cyclic voltammograms (CVs) for the first three cycles were plotted in Figure 4. In the first cathodic sweep for the cell containing  $\text{Zn}_2\text{GeO}_4$ , a sharp peak at 0.7 V vs.  $\text{Li}/\text{Li}^+$  corresponded to a combination of the reduction/decomposition of  $\text{Zn}_2\text{GeO}_4$ , the formation of solid electrolyte interphase (SEI), and the formation of  $\text{Li}_x\text{Zn}$  alloy (see Figure 4a). At potentials below 0.3 V vs.  $\text{Li}/\text{Li}^+$ , another peak arose as the result of the formation of  $\text{Li}_x\text{Ge}$  alloy.<sup>[42,43]</sup> Upon delithiation, two peaks appeared, centred at ca. 0.5 and 1.1 V vs.  $\text{Li}/\text{Li}^+$ . They were previously been assigned to the delithiation of the  $\text{Li}_x\text{Ge}$  alloy and the combined delithiation of the  $\text{Li}_x\text{Zn}$  as well as the partial oxidation of Zn and Ge, respectively.<sup>[42,43]</sup> This means that the lithiation and delithiation mechanism could be broadly expected to be as follows (see Equations 4 to 8);







(Lithiation/delithiation, reversible: Eq. 8)

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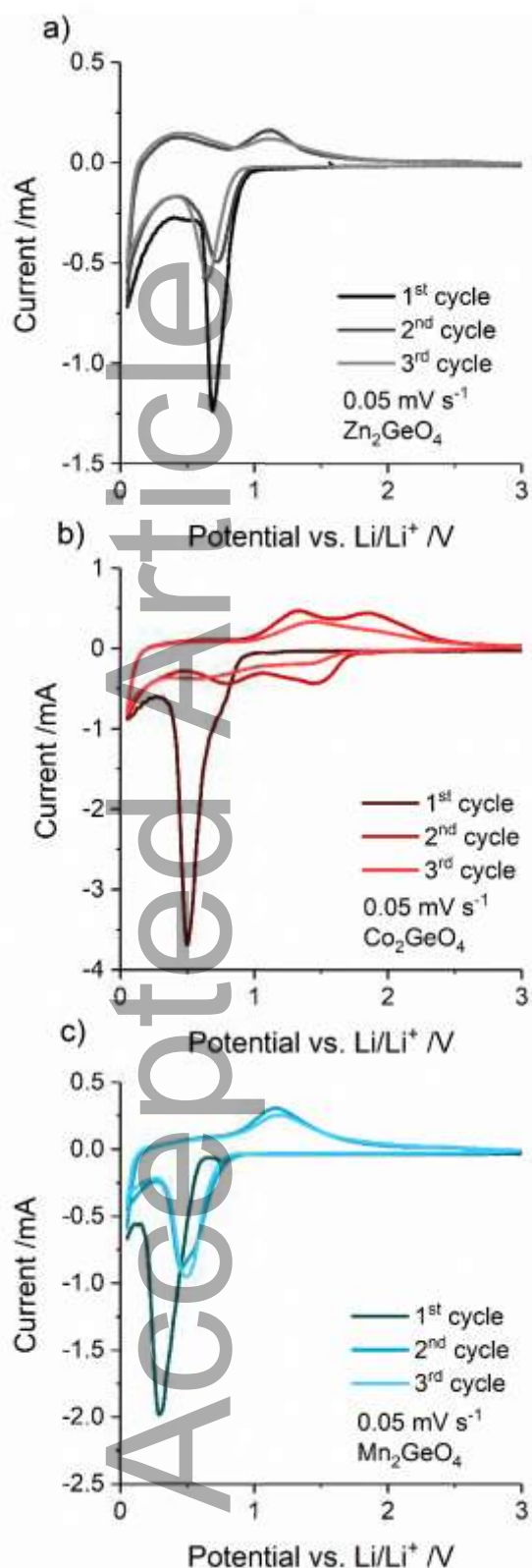


Figure 5: First three cycles of the cyclic voltammeteries at a scan rate of  $0.05 \text{ mV s}^{-1}$  for a)  $\text{Zn}_2\text{GeO}_4$ , b)  $\text{Co}_2\text{GeO}_4$ , and c)  $\text{Mn}_2\text{GeO}_4$ .

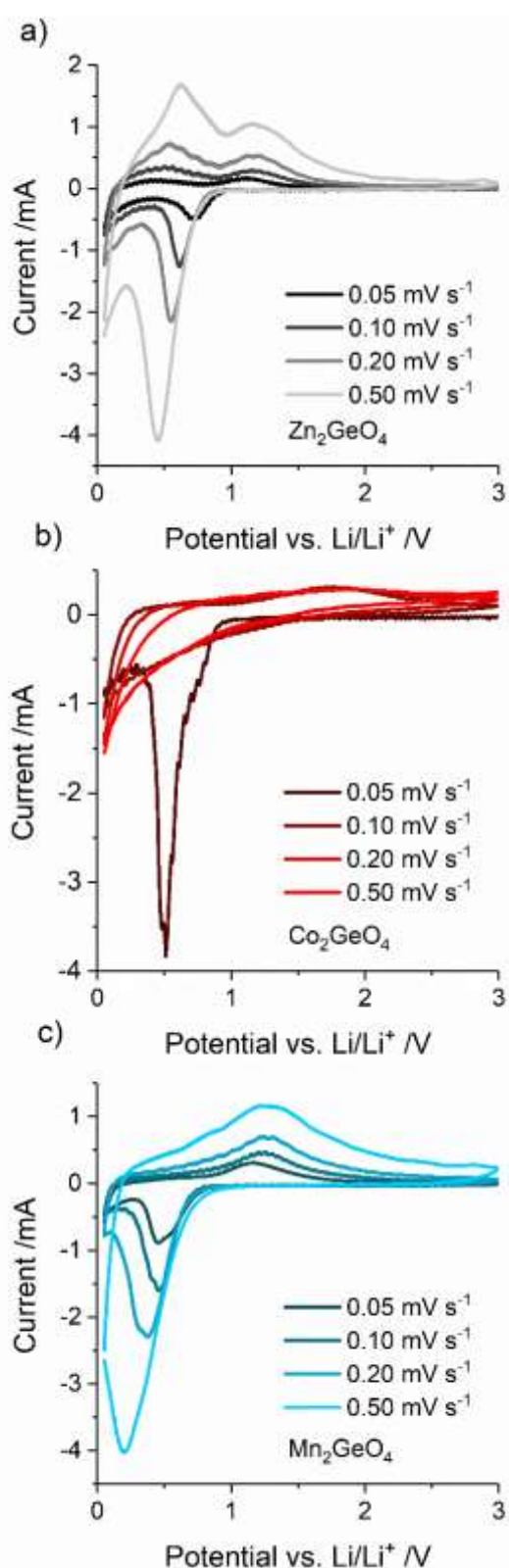
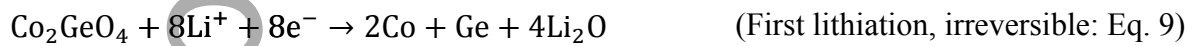


Figure 5: Cyclic voltammeteries at the range of scan rates  $0.05$  to  $0.50 \text{ mV s}^{-1}$  for a)  $\text{Zn}_2\text{GeO}_4$ , b)  $\text{Co}_2\text{GeO}_4$ , and c)  $\text{Mn}_2\text{GeO}_4$ .

The reversibility of the process could be seen in the similarity of the plots for the

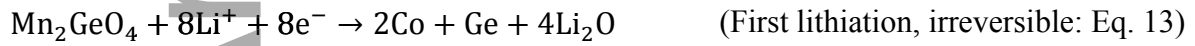
second and third cycles. There was a significant shift in peak position for the first cathodic peak in the second cycle compared to the first cycle, which indicated the different lithiation process occurring (GeO<sub>2</sub> and ZnO reduction instead of Zn<sub>2</sub>GeO<sub>4</sub> decomposition).

The CV for the first cycle of the cell containing Co<sub>2</sub>GeO<sub>4</sub> revealed a major peak at ca. 0.6 V vs. Li/Li<sup>+</sup> during the first lithiation, which has previously been associated with the decomposition of Co<sub>2</sub>GeO<sub>4</sub>, the formation of an SEI layer, and the alloying reaction of Li<sub>x</sub>Ge.<sup>[20]</sup> Upon delithiation, two peaks appeared in the CV at ca. 1.2 and 2.0 V vs. Li/Li<sup>+</sup> (see Figure 4b). The peak at lower potential was assigned as the delithiation and re-oxidation of Ge, whereas the peak at higher potential was associated with re-oxidation of Co to CoO. However, the reversibility for this process was not as substantive as that for the cell containing Zn<sub>2</sub>GeO<sub>4</sub>. During the second lithiation of the cell containing Co<sub>2</sub>GeO<sub>4</sub>, there were peaks at ca. 1.5 and 0.9 V vs. Li/Li<sup>+</sup>, which is in agreement with previous reports in the literature.<sup>[20]</sup> The whole lithiation and delithiation process for the cobalt germanate could, therefore, be described as follows;



For the cell containing Mn<sub>2</sub>GeO<sub>4</sub>, the first lithiation (cathodic sweep) showed a very small and a very large peak at ca. 0.7 and 0.3 V vs. Li/Li<sup>+</sup>, respectively. The small peak was assigned to the formation of a SEI layer,<sup>[11,23]</sup> whereas the major peak was ascribed to the decomposition of Mn<sub>2</sub>GeO<sub>4</sub> and the alloying of Li<sub>x</sub>Ge. Interestingly, the decomposition of Mn<sub>2</sub>GeO<sub>4</sub> occurred at significantly lower potentials vs. Li/Li<sup>+</sup> than for M<sub>2</sub>GeO<sub>4</sub> (M = Co or

Zn). Upon delithiation, there was a single peak at ca. 1.2 V vs. Li/Li<sup>+</sup>, which could be associated with the re-oxidation of Ge<sup>[11,23]</sup>, however, the same potential has previously also been assigned as the re-oxidation of Mn to MnO.<sup>[44]</sup> Upon the second lithiation, the single peak shifted to ca. 0.5 V vs. Li/Li<sup>+</sup>, similar to the potential reported for the cathodic peak in the second cycle for Zn<sub>2</sub>GeO<sub>4</sub>. This suggested that in this case, the peak could be associated with the reduction of both GeO<sub>2</sub> and MnO as well as the alloying reaction for Li<sub>x</sub>Ge. Thereafter, peak shapes and sizes remained similar, indicating good reversibility. The whole lithiation and delithiation process could therefore be described as follows;



To further elucidate the potentiodynamic properties of the different metal germanates, the Li-ion half-cells were cycled in the range of scan rates 0.05 to 10.0 mV s<sup>-1</sup>. Except for a shift in the peak positions due to higher overpotentials, the shapes of the CVs for Zn<sub>2</sub>GeO<sub>4</sub> remained constant, indicating good rate properties (see Figure 5a). At a scan rate of 0.50 mV s<sup>-1</sup>, the lithiation peak had shifted to ca. 0.50 V vs. Li/Li<sup>+</sup>, whereas the delithiation peaks had shifted to ca. 0.55 and 1.10 V vs. Li/Li<sup>+</sup>.

The scan rate tests for the half-cell with Co<sub>2</sub>GeO<sub>4</sub> revealed poor rate performance; the peaks for Co and Ge re-oxidation disappeared almost completely at a scan rate of 0.50 mV s<sup>-1</sup> (see Figure 5b). The CVs for the cell containing Mn<sub>2</sub>GeO<sub>4</sub> at different scan rates revealed excellent rate performance and significant peak broadening (see Figure 5c). The good rate performance of M<sub>2</sub>GeO<sub>4</sub> (M = Zn or Mn) compared to Co<sub>2</sub>GeO<sub>4</sub> resulted in higher specific

capacities at higher scan rates (see Figure S6). For example, at a scan rate of  $1.0 \text{ mV s}^{-1}$ , the specific capacities were ca. 480, 50, and  $305 \text{ mAh g}^{-1}$  for  $\text{M}_2\text{GeO}_4$  ( $\text{M} = \text{Zn}, \text{Co}$  and  $\text{Mn}$ , respectively). Whilst the CVs for  $\text{M}_2\text{GeO}_4$  ( $\text{M} = \text{Zn}$  or  $\text{Mn}$ ) showed significant peaks even at a scan rate of  $10.0 \text{ mV s}^{-1}$ , the CV for  $\text{Co}_2\text{GeO}_4$  showed barely any charge storage (see Figure S7).

The charge storage properties of the three metal germanate containing half-cells were further investigated using galvanostatic charge/discharge cycling (see Figure 6). All the cells showed a similar specific delithiation capacity in the first cycle. They were ca. 650, 660, and  $725 \text{ mAh g}^{-1}$  for the cells containing  $\text{M}_2\text{GeO}_4$ , ( $\text{M} = \text{Zn}, \text{Co}, \text{Mn}$ ), respectively, at a specific current of  $0.1 \text{ A g}^{-1}$ . For all cells, Coulombic efficiencies for the first cycle were  $< 60 \%$  due to first cycle losses from the irreversible decomposition of the initial  $\text{M}_2\text{GeO}_4$  compounds, the formation of an SEI, and other irreversible processes. Whilst the cells containing  $\text{Zn}_2\text{GeO}_4$  and  $\text{Mn}_2\text{GeO}_4$  showed stable cycling (specific capacities falling to ca. 600 and  $510 \text{ mAh g}^{-1}$

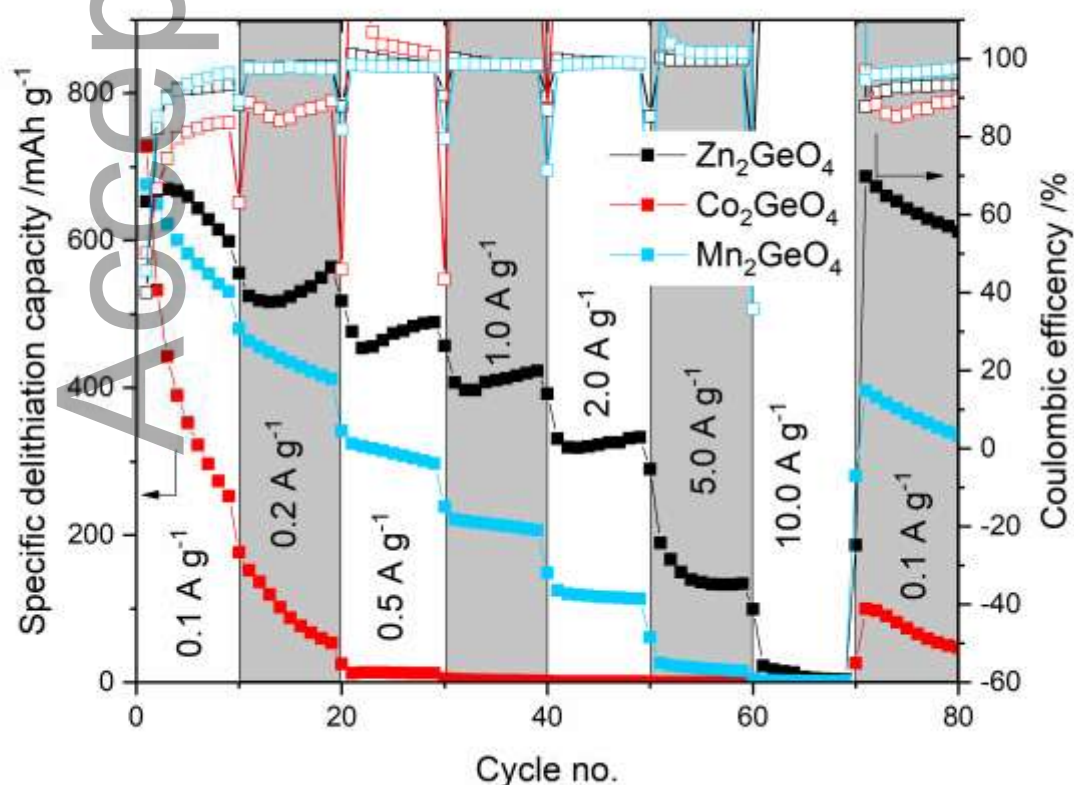


Figure 6: Specific delithiation (charge) capacities of the galvanostatic C-rate tests for the three germanates (left axis) along with the corresponding Coulombic efficiencies (right axis).

mAh g<sup>-1</sup>, respectively for 10 cycles at 0.1 A g<sup>-1</sup>), the specific capacity of the cell containing Co<sub>2</sub>GeO<sub>4</sub> fell to ca. 240 mAh g<sup>-1</sup>. The same cell for Co<sub>2</sub>GeO<sub>4</sub> also showed significantly poorer rate performance than the other samples. Furthermore, whilst the cell containing Co<sub>2</sub>GeO<sub>4</sub> did not store any charge at a specific current of 1.0 A g<sup>-1</sup>, cells containing M<sub>2</sub>GeO<sub>4</sub> (M = Zn and Mn) still showed specific capacities of ca. 420 and 220 mAh g<sup>-1</sup>, respectively. Even at a specific capacity of 2.0 A g<sup>-1</sup>, the cells with M<sub>2</sub>GeO<sub>4</sub> (M = Zn and Mn) showed specific capacities of 350 and 130 mAh g<sup>-1</sup>, respectively. After cycling cells at different current rates up to 10 A g<sup>-1</sup>, the current rate was returned to 0.1 A g<sup>-1</sup>, yielding specific capacities of 660, 380, and 80 mAh g<sup>-1</sup> for the cells containing the metal germinates M<sub>2</sub>GeO<sub>4</sub>, (where M= Zn, Mn and Co), respectively.

The first three cycles of galvanostatic charge/discharge cycling at a specific current of 0.1 A g<sup>-1</sup> were plotted in **Error! Reference source not found.** For the cell containing Zn<sub>2</sub>GeO<sub>4</sub>, in the first cycle, the lithiation confirmed the process as described for the CVs above (see **Error! Reference source not found.**a); a plateau at ca. 0.9 V vs. Li/Li<sup>+</sup> indicated the decomposition of Zn<sub>2</sub>GeO<sub>4</sub>, whereas the additional capacity in the sloped part of the curve at potentials below 0.9 V vs. Li/Li<sup>+</sup> incorporated the alloying of Zn and Ge with Li. During the delithiation, there were two distinct slopes, the one at lower potentials vs. Li/Li<sup>+</sup> caused by the delithiation of Li<sub>x</sub>Ge and the one at higher potentials vs. Li/Li<sup>+</sup> caused by the delithiation of Li<sub>x</sub>Zn and the re-oxidation of Ge and Zn. The second and third lithiation and delithiation curves were nearly identical, indicating excellent reversibility. For the cell containing Co<sub>2</sub>GeO<sub>4</sub>, the lithiation in the first cycle showed a region with a gentle slope in the range of potentials 0.9 to 0.6 V vs. Li/Li<sup>+</sup>, which could be ascribed to the decomposition of Co<sub>2</sub>GeO<sub>4</sub>. However, the comparison between the first three cycles and the capacity fade during these cycles showed the poor reversibility of the lithiation and delithiation. For the cell containing Mn<sub>2</sub>GeO<sub>4</sub>, the first lithiation showed a plateau at ca. 0.5 V vs. Li/Li<sup>+</sup>, which could

be ascribed to the decomposition of  $\text{Mn}_2\text{GeO}_4$ . The decomposition of  $\text{Mn}_2\text{GeO}_4$  occurred at lower potentials than those of  $\text{M}_2\text{GeO}_4$  ( $\text{M} = \text{Zn}$  or  $\text{Co}$ ), as previously observed from the potentiodynamic measurements. Upon subsequent delithiation, a region with a gentle slope in the region 1.0 to 1.4 V vs.  $\text{Li/Li}^+$  suggested the re-oxidation of Mn and Ge, whereas the region below 1.0 V vs.  $\text{Li/Li}^+$ , (with a steeper slope), could be ascribed to the delithiation of  $\text{Li}_x\text{Ge}$ . The reversibility of the lithiation and delithiation reactions of  $\text{Mn}_2\text{GeO}_4$  were confirmed by the small differences between the charge/discharge curves of different cycles.

An analysis of the galvanostatic charge/discharge curves at varying specific currents was conducted (see Figure 8). The charge/discharge curves for the fifth cycle at  $0.1 \text{ A g}^{-1}$  and for the fifth cycle after returning the specific current to  $0.1 \text{ A g}^{-1}$  after testing at different specific currents (dashed line) were nearly identical for

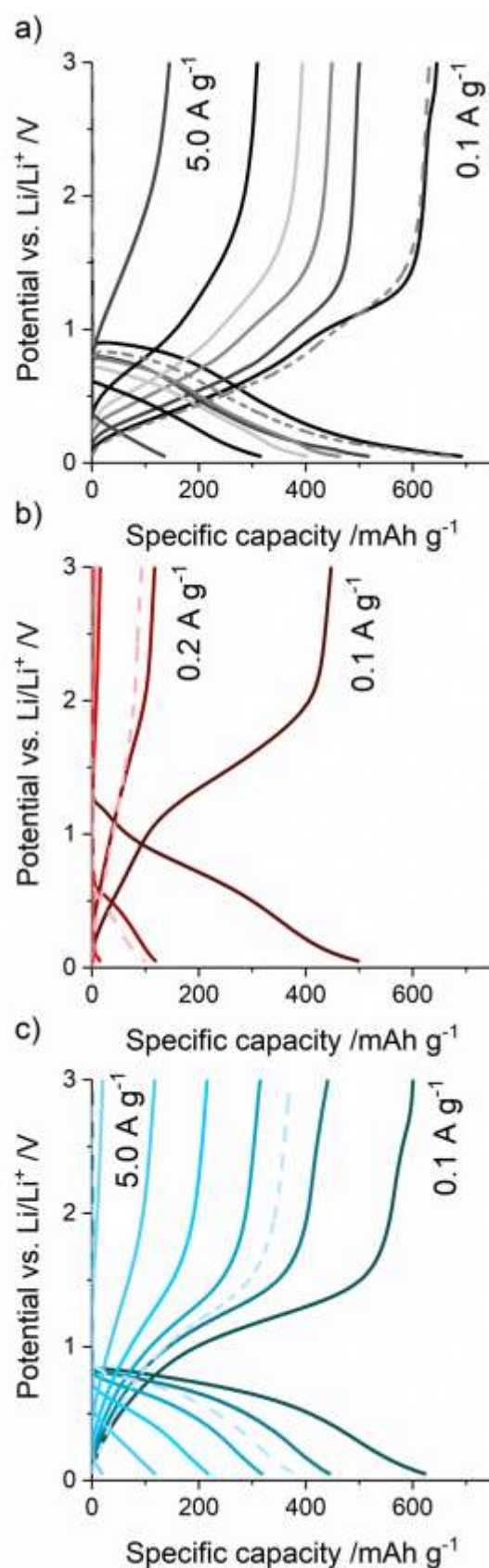


Figure 7: Charge/discharge curves at varying specific currents ( $0.1\text{--}5.0 \text{ A g}^{-1}$ ) for a)  $\text{Zn}_2\text{GeO}_4$ , b)  $\text{Co}_2\text{GeO}_4$ , and c)  $\text{Mn}_2\text{GeO}_4$ .



$\text{Zn}_2\text{GeO}_4$  (see Figure 8a), indicating excellent reversibility. The cyclability of the cell containing  $\text{Co}_2\text{GeO}_4$  was much poorer (see Figure 8b), whereas that for the cell containing  $\text{Mn}_2\text{GeO}_4$  (see Figure 8c) was intermediate. At higher specific currents, the shape of the curves did not significantly differ for  $\text{Zn}_2\text{GeO}_4$  in the specific current range  $0.1$  to  $1.0 \text{ A g}^{-1}$ . Even at  $1.0 \text{ A g}^{-1}$ , the delithiation curve still showed evidence of the two contributors to specific capacity. For  $\text{Co}_2\text{GeO}_4$ , on the other hand, the gentle slope in the range  $1.0$  to  $2.0 \text{ V}$  vs.  $\text{Li/Li}^+$  during the discharge at  $0.1 \text{ A g}^{-1}$  disappeared almost completely even at  $0.2 \text{ A g}^{-1}$ . For  $\text{Mn}_2\text{GeO}_4$ , the contribution factors to the delithiation capacity were still observable even at  $1.0 \text{ A g}^{-1}$ , although the specific capacity had fallen to ca.  $190 \text{ mAh g}^{-1}$ .

To further analyse the cycling stability of the different samples, half-cells were cycled

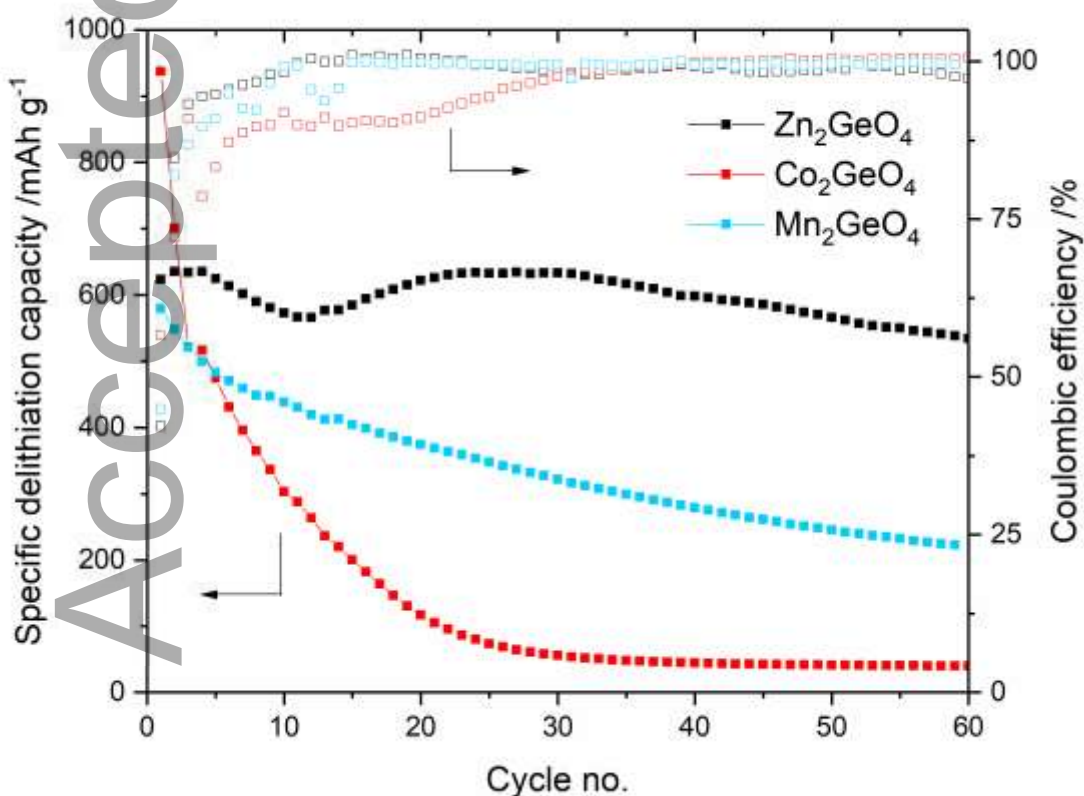


Figure 8: Long term galvanostatic cycling for the three metal germanates at a specific current of  $0.1 \text{ A g}^{-1}$ .



at a specific current of  $0.1 \text{ A g}^{-1}$  for 60 cycles (see Figure 9). The cell containing  $\text{Zn}_2\text{GeO}_4$  showed superior cycling stability compared to the others. The specific capacity of  $\text{Zn}_2\text{GeO}_4$  fell from  $625 \text{ mAh g}^{-1}$  in the first cycle to  $540 \text{ mAh g}^{-1}$  after 60 cycles, indicating a capacity retention of ca. 87 %. For cells containing  $\text{M}_2\text{GeO}_4$  ( $\text{M} = \text{Co}$  or  $\text{Mn}$ ), the initial specific capacities were 935 and  $580 \text{ mAh g}^{-1}$ , respectively. After 60 cycles, these fell to 40 and  $225 \text{ mAh g}^{-1}$ , respectively, indicating capacity losses of ca. 95 and 61 %, respectively. Alloying materials reported in the literature often suffer from poor reversibility and rate performance. For example, a comparison of ball-milled and commercial nanoparticulate Si as negative electrode materials showed that the specific discharge capacities fell from ca. 2700 and  $2600 \text{ mAh g}^{-1}$  for ball-milled and commercial Si to ca. 850 and  $500 \text{ mAh g}^{-1}$ , respectively, after 20 cycles (at a rate of C/20).<sup>[45]</sup> Attempts to improve the performance of alloying materials often require more complicated syntheses and the introduction of additional active phases. For example, Si/ $\text{TiO}_2$  composites have been explored and showed improved capacity retention. Nevertheless, the capacity retention after 50 cycles was still only 14, 23, and 34 % for Si: $\text{TiO}_2$  molar ratios of 1:1, 1:2, and 1:4, respectively.<sup>[46]</sup> Si wrapped in  $\text{V}_2\text{O}_5$  nanosheets has been explored, but even for these the specific capacity fell from ca. 900 to  $550 \text{ mAh g}^{-1}$  over 20 cycles at a specific current of  $0.5 \text{ A g}^{-1}$  (after having been cycled at varying specific currents for 30 cycles).<sup>[47]</sup>

Furthermore, electrochemical impedance spectroscopy (EIS) was conducted, both for freshly made half-cells and for half-cells that had been cycled galvanostatically for 30 cycles at a specific current of  $0.1 \text{ A g}^{-1}$ . Before cycling,  $\text{M}_2\text{GeO}_4$  ( $\text{M} = \text{Co}$  or  $\text{Mn}$ ) appeared to have similarly low charge transfer resistance (see Figure S8a), whereas the charge transfer resistance of the cell containing  $\text{Zn}_2\text{GeO}_4$  was slightly higher. After cycling, the charge transfer resistance increased for all samples. However, whilst the increase in charge transfer resistances seemed fairly limited for  $\text{Zn}_2\text{GeO}_4$  and  $\text{Mn}_2\text{GeO}_4$  (which showed very similar

charge transfer resistances after cycling), the increase for  $\text{Co}_2\text{GeO}_4$  was significantly larger. This might explain the poor cycling stability as well as the poor rate properties of the material.

## Conclusions

Nanosized metal germanates ( $\text{M}_2\text{GeO}_4$ ;  $\text{M} = \text{Co}, \text{Mn}, \text{Zn}$ ) samples were successfully synthesised via a continuous hydrothermal flow synthesis method for the first time. The products showed a diverse range of morphologies and crystal structures. Phase pure rhombohedral  $\text{Zn}_2\text{GeO}_4$  nanorods, cubic spinel  $\text{Co}_2\text{GeO}_4$  nanoparticles, and orthorhombic  $\text{Mn}_2\text{GeO}_4$  nanotubes/nanoparticles were synthesised. The samples were analysed electrochemically as negative electrodes for Li-ion half-cells and the different reaction mechanisms described and contrasted.  $\text{Zn}_2\text{GeO}_4$  showed excellent performance, due to its morphology and the alloying and conversion mechanisms of both Zn and Ge. After 10 and 60 cycles (at a specific current of  $0.1 \text{ A g}^{-1}$ ),  $\text{Zn}_2\text{GeO}_4$  showed a specific capacity of 600 and 540  $\text{mAh g}^{-1}$ , respectively, in excess of the maximum theoretical capacity of commercial graphite anodes ( $372 \text{ mAh g}^{-1}$ ). At higher specific currents, e.g.  $2.0 \text{ A g}^{-1}$ ,  $\text{Zn}_2\text{GeO}_4$  still retained a specific capacity of  $350 \text{ mAh g}^{-1}$ , indicating excellent rate properties.

For the first time,  $\text{Mn}_2\text{GeO}_4$  was studied as a potential active material for Li-ion battery negative electrodes. It showed good performance at a specific current of  $0.1 \text{ A g}^{-1}$ , with a specific capacity of  $510 \text{ mAh g}^{-1}$  after 10 cycles.  $\text{Mn}_2\text{GeO}_4$  also showed good rate performance, with a specific capacity of  $220 \text{ mAh g}^{-1}$  at a specific current of  $1.0 \text{ A g}^{-1}$ . The good electrochemical properties were argued to be a result of both the alloying and conversion reactions of Ge and the conversion reaction of Mn. Therefore, it has been shown that continuous hydrothermal synthesis presents an excellent method for the scalable synthesis of nanosized germanates. Furthermore, we have shown that some of these

germanates are promising materials for negative electrode materials in LIBs and that whilst some germanates such as  $\text{Zn}_2\text{GeO}_4$  have received widespread attention, others such as  $\text{Mn}_2\text{GeO}_4$  have been underexplored and offer promise for future research.

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## References

- [1] M. Armand, J.-M. Tarascon, *Nature* **2008**, *451*, 652–657.
- [2] M. R. Palacín, *Chem. Soc. Rev.* **2009**, *38*, 2565–2575.
- [3] P. G. Bruce, B. Scrosati, J.-M. Tarascon, *Angew. Chemie Int. Ed.* **2008**, *47*, 2930–2946.
- [4] K. Tang, X. Mu, P. a. van Aken, Y. Yu, J. Maier, *Adv. Energy Mater.* **2013**, *3*, 49–53.
- [5] P. V. Braun, J. Cho, J. H. Pikul, W. P. King, H. Zhang, *Curr. Opin. Solid State Mater. Sci.* **2012**, *16*, 186–198.
- [6] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria, C. Capiglia, *J. Power Sources* **2014**, *257*, 421–443.
- [7] M. Ge, J. Rong, X. Fang, C. Zhou, *Nano Lett.* **2012**, *12*, 2318–2323.
- [8] Z.-W. Fu, F. Huang, Y. Zhang, Y. Chu, Q.-Z. Qin, *J. Electrochem. Soc.* **2003**, *150*, A714.
- [9] R. A. Huggins, *J. Power Sources* **1999**, *81–82*, 13–19.
- [10] W. J. Zhang, *J. Power Sources* **2011**, *196*, 877–885.
- [11] Y. Feng, X. Li, Z. Shao, H. Wang, *J. Mater. Chem. A* **2015**, *3*, 15274–15279.
- [12] S. Yuvaraj, R. K. Selvan, Y. S. Lee, *RSC Adv.* **2016**, *6*, 21448–21474.
- [13] N. Liu, H. Wu, M. T. McDowell, Y. Yao, C. Wang, Y. Cui, *Nano Lett.* **2012**, *12*, 3315–3321.
- [14] J. Cabana, L. Monconduit, D. Larcher, M. R. Palacín, *Adv. Mater.* **2010**, *22*, E170–E192.
- [15] L. Croguennec, M. R. Palacin, *J. Am. Chem. Soc.* **2015**, *137*, 3140–3156.
- [16] Y. M. Lin, K. C. Klavetter, A. Heller, C. B. Mullins, *J. Phys. Chem. Lett.* **2013**, *4*, 999–1004.
- [17] J. Graetz, C. C. Ahn, R. Yazami, B. Fultz, *J. Electrochem. Soc.* **2004**, *151*, A698.
- [18] T. Song, Y. Jeon, M. Samal, H. Han, H. Park, J. Ha, D. K. Yi, J. M. Choi, H. Chang, Y. M. Choi, et al., *Energy Environ. Sci.* **2012**, *5*, 9028–9033.
- [19] W. Liang, H. Yang, F. Fan, Y. Liu, X. H. Liu, J. Y. Huang, T. Zhu, S. Zhang, *ACS Nano* **2013**, *7*, 3427–3433.
- [20] S. Jin, G. Yang, H. Song, H. Cui, C. Wang, *ACS Appl. Mater. Interfaces* **2015**, *7*,

- 24932–24943.
- [21] J. S. Peña, I. Sandu, O. Joubert, F. S. Pascual, C. O. Areán, T. Brousse, *Electrochem. Solid-State Lett.* **2004**, *7*, A278.
  - [22] W. Chen, L. Lu, S. Maloney, Y. Yang, W. Wang, *Phys. Chem. Chem. Phys.* **2015**, *17*, 5109–5114.
  - [23] F. Zou, X. Hu, L. Qie, Y. Jiang, X. Xiong, Y. Qiao, Y. Huang, *Nanoscale* **2014**, *6*, 924–930.
  - [24] Q. Li, X. Miao, C. Wang, L. Yin, *J. Mater. Chem. A* **2015**, *3*, 21328–21336.
  - [25] R. Wang, S. P. Wu, Y. C. Lv, Z. Q. Lin, *Langmuir* **2014**, *30*, 8215–8220.
  - [26] J. K. Feng, M. O. Lai, L. Lu, *Electrochem. commun.* **2011**, *13*, 287–289.
  - [27] W. Chen, S. Maloney, W. Wang, *Electrochim. Acta* **2015**, *176*, 96–102.
  - [28] J. A. Darr, J. Zhang, N. M. Makwana, X. Weng, *Chem. Rev.* **2017**, *117*, 11125–11238.
  - [29] R. I. Gruar, C. J. Tighe, J. A. Darr, *Ind. Eng. Chem. Res.* **2013**, *52*, 5270–5281.
  - [30] D. Bauer, A. J. Roberts, C. L. Starkey, R. Vedarajan, D. J. L. Brett, P. R. Shearing, N. Matsumi, J. A. Darr, *Int. J. Electrochem. Sci.* **2018**, *13*, 5120–5140.
  - [31] D. Bauer, A. J. Roberts, S. G. Patnaik, D. J. L. Brett, P. R. Shearing, E. Kendrick, N. Matsumi, J. A. Darr, *J. Electrochem. Soc.* **2018**, *165*, A1662–A1670.
  - [32] D. Bauer, A. J. Roberts, N. Matsumi, J. A. Darr, *Nanotechnology* **2017**, *28*, 195403.
  - [33] J. A. Darr, C. J. Tighe, R. I. Gruar, *Co-Current Mixer, Apparatus, Reactor and Method for Precipitating Nanoparticles*, **2013**, US2013/0136687 A1.
  - [34] C. J. Denis, C. J. Tighe, R. I. Gruar, N. M. Makwana, J. A. Darr, *Cryst. Growth Des.* **2015**, *15*, 4256–4265.
  - [35] S. Jin, G. Yang, H. Song, H. Cui, C. Wang, *ACS Appl. Mater. Interfaces* **2015**, *7*, 24932–24943.
  - [36] U. Holzwarth, N. Gibson, *Nat. Nanotechnol.* **2011**, *6*, 534–534.
  - [37] S. Yan, L. Wan, Z. Li, Z. Zou, *Chem. Commun.* **2011**, *47*, 5632.
  - [38] S. Wu, Z. Wang, X. Ouyang, Z. Lin, *Nanoscale* **2013**, *5*, 12335–12341.
  - [39] X. Ge, S. Song, H. Zhang, *CrystEngComm* **2012**, *14*, 7306.
  - [40] J. Liu, G. Zhang, J. C. Yu, Y. Guo, *Dalt. Trans.* **2013**, *42*, 5092.
  - [41] M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.* **2011**, *257*, 2717–2730.
  - [42] Y. Chen, Y. Lin, N. Du, C. Xiao, S. Wu, Y. Zhang, D. Yang, *Energy Technol.* **2017**, *5*, 1656–1662.
  - [43] R. Yi, J. Feng, D. Lv, M. L. Gordin, S. Chen, D. Choi, D. Wang, *Nano Energy* **2013**, *2*, 498–504.
  - [44] J. Chen, Y. Wang, X. He, S. Xu, M. Fang, X. Zhao, Y. Shang, *Electrochim. Acta* **2014**, *142*, 152–156.
  - [45] I. Sandu, P. Moreau, D. Guyomard, T. Brousse, L. Roué, *Solid State Ionics* **2007**, *178*, 1297–1303.
  - [46] Y. Yang, Y. Bai, S. Zhao, Q. Chang, W. Zhang, *J. Alloys Compd.* **2013**, *579*, 7–11.
  - [47] G. Carbonari, F. Maroni, A. Birrozzi, R. Tossici, F. Croce, F. Nobili, *Electrochim. Acta* **2018**, *281*, 676–683.

Continuous hydrothermal flow synthesis of nanosized metal germanates ( $M_2\text{GeO}_4$ ;  $M = \text{Co}$ ,  $\text{Mn}$ ,  $\text{Zn}$ ) has been conducted for the first time. These materials show both alloying and conversion reactions associated with Ge and impressive specific capacities of  $600 \text{ mAh g}^{-1}$  ( $\text{Zn}_2\text{GeO}_4$ ),  $510 \text{ mAh g}^{-1}$  ( $\text{Mn}_2\text{GeO}_4$ ) and  $240 \text{ mAh g}^{-1}$  ( $\text{Co}_2\text{GeO}_4$ ).

